

The invention relates to novel compositions for the oxidation dyeing of keratin fibres, comprising at least one para-phenylenediamine derivative containing an azetidinyI group as oxidation base, to the dyeing process and to the dyeing kit using this composition, and also to novel para-phenylenediamines containing an azetidinyI group.

It is known practice to dye keratin fibres, and in particular human hair, with dye compositions containing oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic compounds such as diaminopyrazole derivatives which are generally referred to as oxidation bases. Oxidation dye precursors, or oxidation bases, are colourless or weakly coloured compounds which, when combined with oxidizing products, can give rise to coloured compounds and dyes by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or colour modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of molecules used as regards the oxidation bases and the couplers allows a wide range of colours to be obtained.

The so-called "permanent" coloration obtained

09890856-1404

5

10

15

25

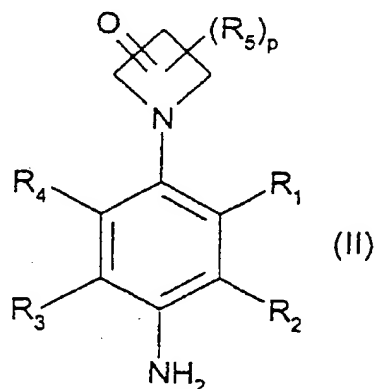
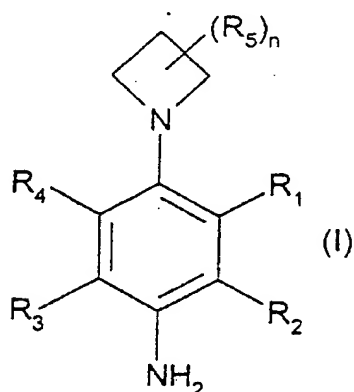
only suitable for use as oxidation bases for the oxidation dyeing of keratin fibres, but also give particularly intense and unselective colorations.

Furthermore, they make it possible to obtain dye

- 5 compositions which give colorations which show good ability to withstand the various attacking factors to which the hair may be subjected.

These discoveries form the basis of the present invention.

- 10 A first subject of the invention is thus a composition for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing, at least one oxidation
- 15 base chosen from para-phenylenediamine derivatives containing an azetidiny group, of formulae (I) and (II) below, and the addition salts thereof with an acid:



- 20 in which:

-  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$  and  $\text{R}_5$ , which may be identical or

09890856-110701

5 N-(C<sub>1</sub>-C<sub>6</sub>)alkylcarbamyl radical; an N,N-di(C<sub>1</sub>-C<sub>6</sub>)-  
alkylcarbamyl radical; an amino radical; a (C<sub>1</sub>-  
C<sub>6</sub>)alkylamino radical; a di(C<sub>1</sub>-C<sub>6</sub>)alkylamino radical; a  
(C<sub>1</sub>-C<sub>6</sub>)alkylcarbonyl radical; a carboxyl radical; a (C<sub>1</sub>-  
C<sub>6</sub>)alkylcarboxyl radical; a (C<sub>1</sub>-C<sub>6</sub>)alkylcarbonyloxy  
0 radical; a C<sub>1</sub>-C<sub>6</sub> trifluoroalkyl radical; a cyano  
radical; a (C<sub>1</sub>-C<sub>6</sub>)alkylthio radical; a formyl radical; a  
radical CH=NHR<sub>6</sub>; or a 5- or 6-membered heterocycle  
containing from 1 to 3 heteroatoms chosen from oxygen,  
nitrogen and sulphur;

```
20 - n is an integer between 1 and 4 inclusive;
    preferably between 1 and 3,
```

it being understood that:

- in formula (I), when  $n = 1$  and when  $R_5$  represents a hydrogen atom and when one of the radicals  $R_1$  to  $R_4$  represents a substituted or unsubstituted amino radical, then at least one of the other radicals  $R_1$  to  $R_4$  is other than a hydrogen atom;

- in formula (I), when  $n = 1$ , and when  $R_5$  represents a hydrogen atom, and when  $R_2$  and  $R_3$  simultaneously represent a hydrogen atom and when one of the radicals  $R_1$  or  $R_4$  also represents a hydrogen atom, a halogen atom, a  $C_1-C_6$  alkyl radical, a  $C_1-C_6$  hydroxyalkyl radical or a  $(C_1-C_6)$ alkoxy $(C_1-C_6)$ alkyl radical, then the other radical  $R_1$  or  $R_4$  cannot represent a substituted or unsubstituted 5-membered heterocycle.

As mentioned above, the colorations obtained with the oxidation dye composition in accordance with the invention are intense and unselective, and also have excellent properties of withstanding the action of various external agents (light, bad weather, washing, permanent waving, perspiration and rubbing). The oxidation dye compositions in accordance with the invention furthermore make it possible to achieve shades in a very broad range of colours.

In formulae (I) and (II) above, the halogen atoms are chosen from bromine, chlorine, iodine and fluorine, and the expression " $C_1-C_6$  alkyl" means a linear or branched alkyl chain containing from 1 to 6 carbon atoms which may be substituted with one or more hydroxyl, amino, acylamino, carbamate or ureido radicals, or optionally with a saturated or unsaturated 5- or 6-membered heterocycle. The hydroxyl and/or amino radicals contained in the said alkyl chain may themselves be unsubstituted or substituted with one or more  $C_1-C_6$  alkyl radicals.

09890856-110701  
FOI/OTI-9580680

Among the para-phenylenediamine derivatives containing an azetidiny1 group, of formulae (I) and (II) above, which may be used as oxidation bases in the dye compositions in accordance with the invention,

5 mention may be made in particular of:

- 4-azetidin-1-ylphenylamine;
- 1-(4-aminophenyl)azetidine-2-carboxylic acid;
- 4-azetidin-1-yl-3-methylphenylamine;
- 1-(4-aminophenyl)azetidine-2-carboxamide;
- 10 - 1-(4-amino-2-methylphenyl)azetidine-2-carboxylic acid;
- 4-azetidin-1-yl-2-methylphenylamine;
- 1-(4-amino-3-methylphenyl)azetidine-2-carboxylic acid;
- 15 - 2-(2-amino-5-azetidin-1-ylphenyl)ethanol;
- 1-[4-amino-3-(2-hydroxyethyl)phenyl]azetidine-2-carboxylic acid;
- 2-(5-amino-2-azetidin-1-ylphenyl)ethanol;
- 1-[4-amino-2-(2-hydroxyethyl)phenyl]azetidine-
- 20 2-carboxylic acid;
- 1-(5-amino-2-azetidin-1-ylphenyl)ethane-1,2-diol;
- 1-[4-amino-2-(1,2-dihydroxyethyl)phenyl]azetidine-2-carboxylic acid;
- 1-(2-amino-5-azetidin-1-ylphenyl)ethane-1,2-diol;
- 25 - 1-[4-amino-3-(1,2-dihydroxyethyl)phenyl]azetidine-2-carboxylic acid;
- 4-azetidin-1-yl-3-dimethylaminomethylphenylamine;
- 1-(4-amino-2-dimethylaminomethylphenyl)azetidine-

09890856-110701  
T040T-9590856

2-carboxylic acid;

- 4-[3-(2-methoxyethoxy)azetidin-1-yl]phenylamine;

- 4-[2-(2-methoxyethoxy)azetidin-1-yl]-3-methyl-phenylamine;

5 - 4-[3-(2-methoxyethoxy)azetidin-1-yl]-2-methyl-phenylamine;

- 4-azetidin-1-yl-3-fluorophenylamine;

- 4-[3-(2-methoxyethoxy)azetidin-1-yl]-3-fluoro-phenylamine;

10 - 1-(aminophenyl)azetidine-4-oxo-2-carboxylic acid;

- 1-(4-aminophenyl)azetidin-3-ol;

- 1-(4-aminophenyl)-3-methylazetidin-3-ol;

- [1-(4-aminophenyl)azetidin-2-yl]methanol;

- [1-(4-aminophenyl)-4-hydroxymethylazetidin-2-yl]-

15 methanol

and the addition salts thereof with an acid.

Among these para-phenylenediamine derivatives containing an azetidiny group, of formulae (I) and (II), the ones that are more particularly preferred

20 are:

- 4-azetidin-1-ylphenylamine;

- 1-(4-aminophenyl)azetidine-2-carboxylic acid;

- 1-(4-aminophenyl)azetidine-2-carboxamide;

- 4-azetidin-1-yl-3-methylphenylamine;

25 - 1-(4-amino-2-methylphenyl)azetidine-2-carboxylic acid;

- 4-azetidin-1-yl-3-dimethylaminomethylphenylamine;

- 2-(5-amino-2-azetidin-1-ylphenyl)ethanol;

09890855 110701

- 1-[4-amino-2-(2-hydroxyethyl)phenyl]azetidine-2-carboxylic acid;
  - 1-(5-amino-2-azetidin-1-ylphenyl)ethane-1,2-diol;
  - 1-[4-amino-2-(1,2-dihydroxyethyl)phenyl]azetidine-2-carboxylic acid;
  - 1-(2-amino-5-azetidin-1-ylphenyl)ethane-1,2-diol;
  - 1-[4-amino-3-(1,2-dihydroxyethyl)phenyl]azetidine-2-carboxylic acid;
  - 1-(4-aminophenyl)azetidin-3-ol;
  - 1-(4-aminophenyl)-3-methylazetidin-3-ol
  - [1-(4-aminophenyl)azetidin-2-yl]methanol
  - [1-(4-aminophenyl)-4-hydroxymethylazetidin-2-yl]methanol;
- and the addition salts thereof with an acid.
- The para-phenylenediamine derivative(s) containing an azetidiny l group, of formulae (I) and/or (II) in accordance with the invention and/or the addition salt(s) thereof with an acid preferably represent from 0.0005% to 12% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005% to 6% by weight approximately relative to this weight.

The medium which is suitable for the dyeing (or the support) generally consists of water or of a mixture of water and at least one organic solvent in order to dissolve the compounds which would not be sufficiently soluble in water. By way of organic solvent, mention may be made, for example, of C<sub>1</sub>-C<sub>4</sub>

09890856-110701



5

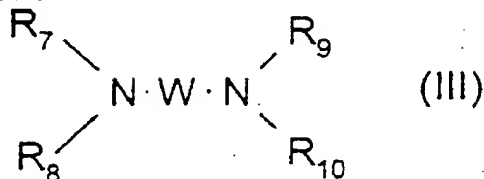
10

15

20

25

hydroxide, potassium hydroxide and the compounds of formula (III) below:



in which W is a propylene residue optionally substituted with a hydroxyl group or a C<sub>1</sub>-C<sub>4</sub> alkyl radical; R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> and R<sub>10</sub>, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radical.

According to one preferred embodiment, the oxidation dye composition in accordance with the invention also contains one or more couplers so as to modify the shades obtained or to enrich them with glints by using the compounds of formulae (I) and/or (II).

The couplers which may be used in the oxidation dye compositions in accordance with the invention may be chosen from the couplers used conventionally in oxidation dyeing, and among which mention may be made in particular of meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers.

These couplers are chosen more particularly from 2-methyl-5-aminophenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxy-

09890856-140701

benzene, 2,4-diamino-1-( $\beta$ -hydroxyethyloxy)benzene,  
 2-amino-4-( $\beta$ -hydroxyethylamino)-1-methoxybenzene,  
 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane,  
 sesamol,  $\alpha$ -naphthol, 2-methyl-1-naphthol, 6-hydroxy-  
 5 indole, 4-hydroxyindole, 4-hydroxy-N-methylindole,  
 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine,  
 1-H-3-methylpyrazol-5-one, 1-phenyl-3-methylpyrazol-  
 5-one, 2-methyl-3-amino-6-methylphenol, 3,5-diamino-  
 2,6-dimethoxypyridine, 6-hydroxybenzomorpholine,  
 10 1,2'-hydroxyethylamino-3'-methylenedioxybenzene and  
 1-methyl-2,6-bis(2'-hydroxyethylamino)benzene, and the  
 addition salts thereof with an acid.

When they are present, the coupler(s)  
 preferably represent(s) from 0.0001% to 10% by weight  
 15 approximately relative to the total weight of the dye  
 composition and even more preferably from 0.005% to 5%  
 by weight approximately relative to this weight.

The dye composition in accordance with the  
 invention may also contain, in addition to the  
 20 compounds of formulae (I) and/or (II) as defined above  
 and the couplers defined above, at least one additional  
 oxidation base, which may be chosen from the oxidation  
 bases conventionally used in oxidation dyeing and among  
 which mention may be made in particular of para-  
 25 phenylenediamines other than the compounds of formulae  
 (I) and (II) in accordance with the invention,  
 bis(phenyl)alkylenediamines, para-aminophenols, ortho-  
 aminophenols and heterocyclic bases, and the addition

T020T" 95906860

salts thereof with an acid.

Among the para-phenylenediamines, mention may be made more particularly, by way of example, of para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis( $\beta$ -hydroxyethyl)-para-phenylenediamine, 4-amino-N,N-bis( $\beta$ -hydroxyethyl)-2-methylaniline, 4-amino-2-chloro-N,N-bis( $\beta$ -hydroxyethyl)aniline, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-( $\beta$ -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl- $\beta$ -hydroxyethyl)-para-phenylenediamine, N-( $\beta,\gamma$ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2- $\beta$ -acetaminoethyloxy-para-phenylenediamine and N-( $\beta$ -methoxyethyl)-para-phenylenediamine, and the addition salts thereof with an acid.

Among the para-phenylenediamines mentioned above, para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyl-

09890855-110701

para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis( $\beta$ -hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2- $\beta$ -acetylaminoethyloxy-para-phenylenediamine and the addition salts thereof with an acid are most particularly preferred.

Among the bis(phenyl)alkylenediamines, mention may be made more particularly, by way of example, of N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4-aminophenyl)-tetramethylenediamine, N,N'-bis(4-methylaminophenyl)-tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

Among the para-aminophenols, mention may be made more particularly, by way of example, of para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-( $\beta$ -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof

09890855-140701

Among the ortho-aminophenols, mention may be made more particularly, by way of example, of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

Among the heterocyclic bases, mention may be made more particularly, by way of example, of pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in patents GB 1,026,978 and GB 1,153,196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-  
15 3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-( $\beta$ -methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid.

Among the pyrimidine derivatives, mention may  
20 be made more particularly of the compounds described,  
for example, in patents DE 2 359 399; JP 88-169 571;  
JP 05 163 124; EP 0 770 375 or patent application  
WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine,  
4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-  
25 4,5,6-triaminopyrimidine, 2,4-dihydroxy-  
5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine, and  
pyrazolopyrimidine derivatives such as those mentioned  
in patent application FR-A-2 750 048, and among which

mention may be made of pyrazolo[1,5-a]pyrimidine-  
 3,7-diamine; 2,5-dimethylpyrazolo[1,5-a]pyrimidine-  
 3,7-diamine; pyrazolo[1,5-a]pyrimidine-3,5-diamine;  
 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine;  
 5 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;  
 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;  
 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol,  
 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol,  
 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxy-  
 10 ethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]-  
 pyrimidin-3-yl)(2-hydroxyethyl)amino]ethanol,  
 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine,  
 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine,  
 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-  
 15 3,7-diamine and 3-amino-5-methyl-7-imidazolylpropyl-  
 aminopyrazolo[1,5-a]pyrimidine, the addition salts  
 thereof with an acid, and the tautomeric forms thereof,  
 when a tautomeric equilibrium exists.

Among the pyrazole derivatives, mention may  
 20 be made more particularly of the compounds described in  
 patents DE 3 843 892, DE 4 133 957 and patent  
 applications WO 94/08969, WO 94/08970, FR-A-2,733,749  
 and DE 195 43 988, such as 4,5-diamino-1-methyl-  
 pyrazole, 4,5-diamino-1-( $\beta$ -hydroxyethyl)pyrazole,  
 25 3,4-diaminopyrazole, 4,5-diamino-  
 1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethyl-  
 pyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-  
 diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dime-

09890856-140701  
 T040T 9506860

- thyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-  
 3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methyl-  
 pyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole,  
 4,5-diamino-1-( $\beta$ -hydroxyethyl)-3-methylpyrazole,  
 5 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-  
 1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-  
 1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-  
 3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-  
 3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-  
 10 3-methyl-1-isopropylpyrazole, 4-amino-  
 5-(2'-aminoethyl)amino-1,3-dimethylpyrazole,  
 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triamino-  
 pyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole  
 and 3,5-diamino-4-( $\beta$ -hydroxyethyl)amino-  
 15 1-methylpyrazole, and the addition salts thereof with  
 an acid.

When they are used, the additional oxidation  
 base(s) preferably represent(s) from 0.0005% to 12% by  
 weight approximately relative to the total weight of  
 20 the dye composition, and even more preferably from  
 0.005% to 6% by weight approximately relative to this  
 weight.

In general, the addition salts with an acid  
 which may be used in the context of the dye  
 25 compositions of the invention (compounds of formulae  
 (I) and (II), couplers and additional oxidation bases)  
 are chosen in particular from the hydrochlorides,  
 hydrobromides, sulphates, citrates, succinates,



tartrates, lactates, phosphates and acetates.

The dye composition in accordance with the invention may also contain one or more direct dyes which may be chosen in particular from dyes of the  
5 nitrobenzene series.

The dye composition in accordance with the invention can also contain various adjuvants used conventionally in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or  
10 zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, inorganic or organic thickeners, antioxidants, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners,  
15 such as, for example, volatile or non-volatile silicones, which are modified or unmodified, film-forming agents, ceramides, preserving agents and opacifiers.

Needless to say, a person skilled in the art  
20 will take care to select this or these optional complementary compound(s) such that the advantageous properties intrinsically associated with the oxidation dye composition in accordance with the invention are not, or not substantially, adversely affected by the  
25 addition or additions envisaged.

The dye composition in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels or any other form which is

09390856-110701

The oxidizing agent present may be chosen from the oxidizing agents conventionally used for the oxidation dyeing of keratin fibres, and among which

mention may be made of hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulphates, and enzymes, among which mention may be made of peroxidases, 2-electron  
5 oxidoreductases such as uricases, and 4-electron oxygenases such as laccases. Hydrogen peroxide is particularly preferred.

09890856-110701  
The pH of the oxidizing composition containing the oxidizing agent as defined above is such  
10 that, after mixing it with the dye composition, the pH of the resulting composition applied to the keratin fibres preferably ranges between 3 and 12 approximately, and even more preferably between 5 and 11. It is adjusted to the desired value by means of  
15 acidifying or basifying agents usually used for the dyeing of keratin fibres and as defined above.

The oxidizing composition as defined above can also contain various adjuvants conventionally used in compositions for dyeing the hair and as defined  
20 above.

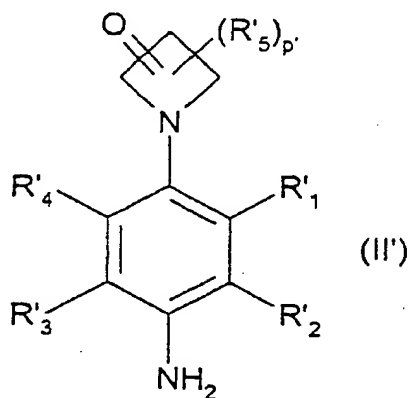
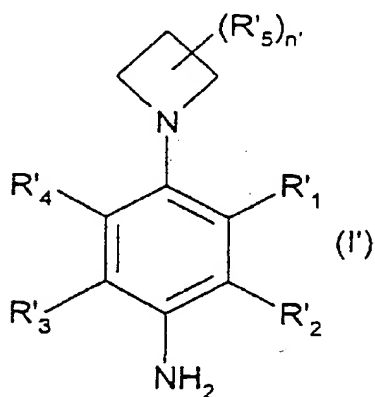
The composition which is finally applied to the keratin fibres can be in various forms, such as in the form of liquids, creams or gels or any other form which is suitable for dyeing keratin fibres, and in  
25 particular human hair.

Another subject of the invention is a multi-compartment device or dyeing "kit" or any other multi-compartment packaging system, a first compartment of

which contains the dye composition as defined above and a second compartment of which contains the oxidizing composition as defined above. These devices may be equipped with a means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

Certain para-phenylenediamine derivatives containing an azetidinyI group, of formulae (I) and (II), used as oxidation bases in the context of the present invention are novel and, in this respect, constitute another subject of the invention.

These novel para-phenylenediamine derivatives containing an azetidinyI group, and also the addition salts thereof with an acid, correspond to the formulae (I') and (II') below:



in which:

-  $R'_1$ ,  $R'_2$ ,  $R'_3$ ,  $R'_4$  and  $R'_5$ , which may be identical or different, represent a hydrogen atom; a halogen atom; a hydroxyl radical; a  $C_1$ - $C_6$  alkyl radical; a  $C_2$ - $C_6$

09890856-110701

alkenyl radical; a  $C_2-C_6$  alkynyl radical; a  $C_1-C_6$  alkoxy radical; a carbamyl radical; a carboxamide radical; an  $N-(C_1-C_6)$  alkylcarbamyl radical; an  $N,N$ -di( $C_1-C_6$ )-alkylcarbamyl radical; an amino radical; a

- 5 (C<sub>1</sub>-C<sub>6</sub>)alkylamino radical; a di(C<sub>1</sub>-C<sub>6</sub>)alkylamino radical; a (C<sub>1</sub>-C<sub>6</sub>)alkylcarbonyl radical; a carboxyl radical; a (C<sub>1</sub>-C<sub>6</sub>)alkylcarboxyl radical; a (C<sub>1</sub>-C<sub>6</sub>)alkylcarbonyloxy radical; a  $C_1-C_6$  trifluoroalkyl radical; a cyano radical; a (C<sub>1</sub>-C<sub>6</sub>)alkylthio radical; a formyl radical; a
- 10 radical  $CH=NHR'_6$ ; or a 5- or 6-membered heterocycle containing from 1 to 3 heteroatoms chosen from oxygen, nitrogen and sulphur;

- $R'_6$  represents a  $C_1-C_6$  alkyl radical; an aromatic ring such as, for example, a phenyl ring, or a 5- or 6-
- 15 membered heteroaromatic ring containing from 1 to 3 heteroatoms chosen from oxygen, nitrogen and sulphur atoms;

- $n'$  is an integer between 1 and 4 inclusive; preferably between 1 and 3,

- 20 -  $p'$  is an integer equal to 1 or 2;

it being understood that:

- in formula (I), when  $n' = 1$  and when  $R'_5$  represents a hydrogen atom and when one of the radicals  $R'_1$  to  $R'_4$  represents a substituted or unsubstituted amino
- 25 radical, then at least one of the other radicals  $R'_1$  to  $R'_4$  is other than a hydrogen atom;

- in formula (I), when  $n' = 1$ , and when  $R'_5$  represents a hydrogen atom, and when  $R'_2$  and  $R'_3$

simultaneously represent a hydrogen atom and when one of the radicals  $R'_1$  or  $R'_4$  also represents a hydrogen atom, a halogen atom, a  $C_1-C_6$  alkyl radical, a  $C_1-C_6$  hydroxyalkyl radical or a  $(C_1-C_6)$ alkoxy $(C_1-C_6)$ alkyl radical, then the other radical  $R'_1$  or  $R'_4$  cannot represent a substituted or unsubstituted 5-membered heterocycle;

with the exclusion of:

- 4-azetidin-1-yl-3-fluorophenylamine;
- 10 - 3-fluoro-4-[3-(2-methoxyethoxy)azetidin-1-yl]-phenylamine;
- diethyl 1-(4-aminophenyl)-2-oxoazetidine-3,3-dicarboxylate;
- diethyl 1-(4-aminophenyl)-2-[1,3]dioxolan-2-yl-4-oxoazetidine-3,3-dicarboxylate;
- 15 - 1-(4-aminophenyl)-4-oxoazetidine-2-carboxylic acid;
- methyl 1-(4-aminophenyl)-4-oxoazetidin-2-yl-methanesulphonate;
- methyl 1-(4-aminophenyl)-4-oxoazetidin-2-yltoluene-20 4-sulphonate.

The compounds specifically excluded from the subject of formulae (I') and (II') above are known in the pharmaceutical field, in particular as antimicrobial agents (see in particular patent application WO 99/12914 and Nicolaus et al., Helvetica Chim. Acta. Vol 48, Issue No. 8, (1965), No. 200-201, pages 1867-1885).

Among the compounds of formulae (I') and

(II') above, mention may be made in particular of:

- 4-azetidin-1-ylphenylamine;
- 1-(4-aminophenyl)azetidine-2-carboxylic acid;
- 1-(4-aminophenyl)azetidine-2-carboxamide;
- 5 - 4-azetidin-1-yl-3-methylphenylamine;
- 1-(4-amino-2-methylphenyl)azetidine-2-carboxylic acid;
- 4-azetidin-1-yl-2-methylphenylamine;
- 1-(4-amino-3-methylphenyl)azetidine-2-carboxylic
- 10 acid;
- 2-(2-amino-5-azetidin-1-ylphenyl)ethanol;
- 1-[4-amino-3-(2-hydroxyethyl)phenyl]azetidine-2-carboxylic acid;
- 2-(5-amino-2-azetidin-1-ylphenyl)ethanol;
- 15 - 1-[4-amino-2-(2-hydroxyethyl)phenyl]azetidine-2-carboxylic acid;
- 1-(5-amino-2-azetidin-1-ylphenyl)ethane-1,2-diol;
- 1-[4-amino-2-(1,2-dihydroxyethyl)phenyl]azetidine-2-carboxylic acid;
- 20 - 1-(2-amino-5-azetidin-1-ylphenyl)ethane-1,2-diol;
- 1-[4-amino-3-(1,2-dihydroxyethyl)phenyl]azetidine-2-carboxylic acid;
- 4-azetidin-1-yl-3-dimethylaminomethylphenylamine;
- 1-(4-amino-2-dimethylaminomethylphenyl)azetidine-
- 25 2-carboxylic acid;
- 4-[3-(2-methoxyethoxy)azetidin-1-yl]phenylamine;
- 4-[2-(2-methoxyethoxy)azetidin-1-yl]-3-methylphenylamine;

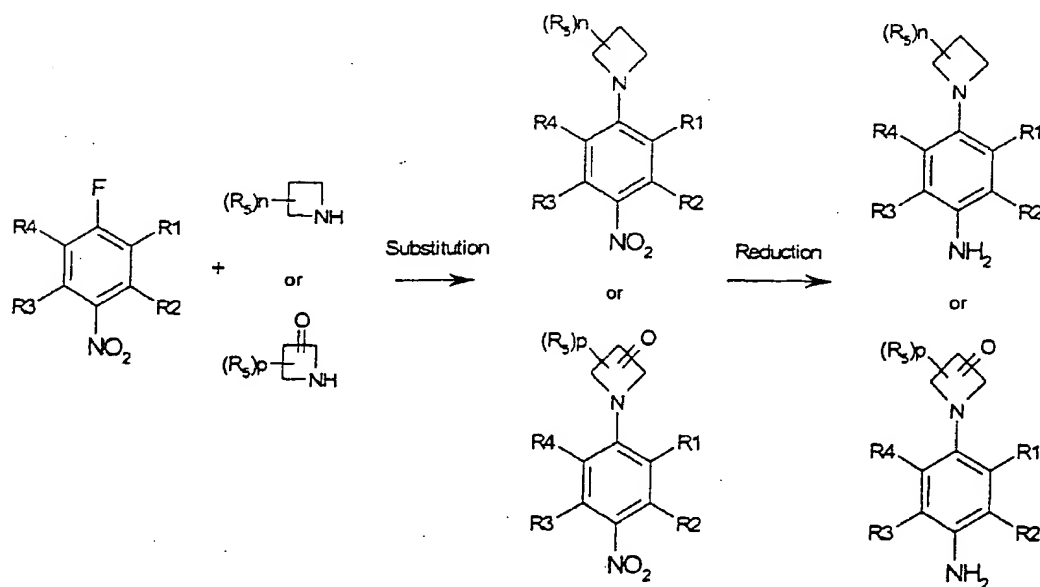
T0207-95805850

- 4-[3-(2-methoxyethoxy)azetidin-1-yl]-2-methyl-phenylamine;
- 1-(4-aminophenyl)azetidin-3-ol
- 1-(4-aminophenyl)-3-methylazetidin-3-ol
- 5 - 1-(4-aminophenol)azetidin-2-yl]methanol
- [1-(4-aminophenyl)-4-hydroxymethylazetidin-2-yl]-methanol

and the addition salts thereof with an acid.

The addition salts with an acid of the  
 10 compounds of formulae (I') and (II') may be chosen from the hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates, phosphates and acetates.

The compounds of formulae (I') and (II') in  
 15 accordance with the invention may be prepared according to the following synthetic scheme:





For the substitution step, methods that are well known in the literature which consist, for example, in carrying out a substitution reaction of an amine of azetidiny1 type on a benzene derivative of p-halonitrobenzene type such as, for example, a p-fluoro-  
 5 nitrobenzene, may be used. Conventional substitution methods as described in the literature are used. The syntheses may be inspired, for example, from the methods described in the following references:

- 10 - Tetrahedron, 51(22), 6167, 1995
- Synthesis, 12, 1147, 1990
- J. Med. Chem., 33(7), 2045, 1990
- J. Chem. Soc. Perkin Trans. 1, 6, 1331, 1988
- J. Chem. Soc. Perkin Trans. 1, 3, 549, 1988
- 15 - Liebigs Ann. Chem., 4, 343, 1988
- Chem. Pharm. Bull., 33(5), 1826, 1985

The nitro derivatives thus obtained may be reduced according to known methods: see in particular R. Hemmer and W. Lürken in Houben-Weyl, "Methoden der  
 20 Organischen Chemie", Vol. E16d, p. 815ff. It will be preferred to use metals such as palladium (Pd), platinum (Pt) or nickel (Ni) in the presence of a hydrogen donor such as ammonium formate, formic acid or cyclohexene instead of hydrogen (S. Ram.  
 25 R.E. Ehrenkaufer, Synthesis, 91, 1988). Metals such as zinc (Zn), tin (Sn) or iron (Fe) may also be used, in acidic medium such as aqueous hydrochloric acid or aqueous acetic acid, optionally with addition of an

00890856-110704

organic solvent such as methanol, ethanol or tetrahydrofuran.

Another subject of the invention is the use of the para-phenylenediamine derivatives containing an azetidiny1 group, of formulae (I), (II), (I') and (II') above, as oxidation bases for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair.

The examples which follow are intended to illustrate the invention without, however, limiting its scope.

#### EXAMPLES

##### Example 1 : Synthesis of 4-azetidin-1-ylphenylamine

a) First-step: preparation of 1-(4-nitrophenyl)-azetidine

20 ml of ethanol and 20 mmol of 1-fluoro-4-nitrobenzene were introduced into a three-necked round-bottomed flask on which was mounted a condenser, an addition funnel and a thermometer, and 22 mmol of azetidine were added over 10 minutes. Stirring was continued for 1 hour.

The crystalline product was filtered off, spin-filtered, washed with alcohol and dried under vacuum.

The expected product was recovered in the form of needles of a bright yellow compound, in a yield of 73%.

00890856-110701

b) Second step: reduction of 1-(4-nitrophenyl)azetidine

2.5 g of 1-(4-nitrophenyl)azetidine obtained above in the preceding step were reduced under hydrogen-transfer conditions in 30 ml of ethanol and 5 30 ml of cyclohexene in the presence of 1 g of palladium-on-charcoal containing 5% water.

The reaction medium was refluxed for one hour, the catalyst was removed by filtration and two equivalents of hydrochloric acid were added at zero 10 degrees. The reduced compound crystallized on dilution with diisopropyl ether. After drying, the expected product was recovered in the form of a white compound, in a yield of 93%.

The  $^1\text{H}$  NMR analysis ( $\text{CD}_3\text{OD}$ )  $\delta$  ppm was as 15 follows: 2.59 (2H, multiplet); 4.43 (4H, triplet); 7.48 (4H, multiplet)

Example 2: Synthesis of the tartrate salt of

1-(4-aminophenyl)-3-hydroxy-3-methylazetidine

20 Step A: preparation of 1-chloro-2,3-epoxy-2-methyl-propane

73.5 ml (0.75 mol) of methallyl chloride are added to 375 ml of water in a 1-litre reactor, followed by addition of 133.5 g (1 eq) of N-bromosuccinimide with vigorous stirring at room temperature.

25 After leaving overnight, the mixture is cooled to  $10^\circ\text{C}$  and aqueous 50% sodium hydroxide (0.75 mol) is added at a rate such that the temperature is maintained at between  $20$  and  $25^\circ\text{C}$ .

09890856-110701  
FOI/OT: 9980660

After 2 hours without stirring, the lower organic phase is separated out and dried over sodium sulphate (10 g), and the organic phase is concentrated. 53.3 g (67%) of crude product are obtained.

5 Separately, the aqueous phase is extracted with dichloromethane and the extracts are dried over sodium sulphate and concentrated. A further 23 g of crude product are obtained. The combined crude product is distilled (60°C/65 mb) to give finally 37.8 g of a  
10 colourless liquid, i.e. a yield of 47%.

**Step B: preparation of 1-diphenylmethyl-3-hydroxy-3-methylazetidine hydrochloride**

28 g (0.263 mol) of 1-chloroepoxy-2-methylpropane are added to a solution of 48.2 g (1 eq) of  
15 diphenylmethylaniline dissolved in 120 ml of methanol. The mixture is stirred for 3 days at room temperature and then for 3 days at reflux. The resulting mixture is cooled and the white precipitate obtained is then filtered off. This product is washed with acetone and  
20 then dried under vacuum over potassium hydroxide to give 46.2 g (61%) of 1-diphenylmethyl-3-hydroxy-3-methylazetidine hydrochloride.

▪ Elemental analysis ( $C_{17}H_{20}NOCl$ ; MW = 289.804)

	% C	% H	% N	% O	% Cl
Theoretical	70.46	6.96	4.83	5.52	12.23
Found	70.36	6.96	5.19	5.89	12.04

**Step C: preparation of 1-(4-nitrophenyl)-3-hydroxy-3-methylazetidine**

36 g (0.124 mol) of 1-diphenylmethyl-3-hydroxy-3-methylazetidine are dissolved in 450 ml of methanol and 15 g of Pd(OH)<sub>2</sub> (20% by weight) are then added. The mixture is placed under a hydrogen pressure of 10 bar at a temperature of 25°C for 2 hours. The catalyst is then filtered off and the solvent is evaporated until a two-phase oil is obtained. The oil obtained is diluted in 100 ml of N-methylpyrrolidone and 17.5 g (1 eq) of 4-fluoronitrobenzene are added, followed by 42.9 g (2.5 eq) of potassium carbonate. The mixture is heated at 95°C for 5 hours and is then poured into 1 l of water. The yellow precipitate obtained is filtered off and washed with water. The crude product is dried under vacuum over potassium hydroxide and is re-slurried in petroleum ether. This product is filtered off, washed with petroleum ether and dried to give 22 g (85%) of 1-(4-nitrophenyl)-3-hydroxy-3-methylazetidine.

▪ Elemental analysis (C<sub>10</sub>H<sub>12</sub>NO<sub>3</sub>; MW = 208.216)

09890856-110701  
FOUOIT-95806860

	% C	% H	% N	% O
Theoretical	57.69	5.81	13.45	23.05
Found	57.29	5.72	13.27	23.08

**Step D: preparation of the tartrate salt of  
1-(4-aminophenyl)-3-hydroxy-3-methylazetidine**

20.8 g (0.1 mol) of 1-(4-nitrophenyl)-  
5 3-hydroxy-3-methylazetidine suspended in 200 ml of  
ethanol are introduced into a hydrogenator in the  
presence of 4 g of wet palladium-on-charcoal. The  
mixture is hydrogenated under a pressure of 6 bar at  
room temperature for a period of 3 hours.

10 After filtering off the catalyst under  
nitrogen, the filtrate is collected in a solution of  
96° ethanol containing 15.1 g (1 eq) of L-tartaric  
acid. The precipitate is filtered off, washed with  
isopropanol and dried under vacuum to give 25.9 g (79%)  
15 of tartrate salt of 1-(4-aminophenyl)-3-hydroxy-  
3-methylazetidine.

▪ Mass spectrum (TSQ 700; ESI-ID):  $m/z = 179$  (MH) +

20 ▪ Elemental analysis (MW = 328.319;  $C_{14}H_{20}N_2O_7$ )

	% C	% H	% N	% O
Theoretical	51.22	6.14	8.53	34.11
Found	50.61	6.44	8.23	34.74

Step 1: preparation of 1-diphenylmethyl-3-hydroxy-azetidine hydrochloride

5                    This compound is obtained according to the  
procedure of Example 2, Step B, starting with 88 g  
(0.480 mol) of diphenylmethylaniline and 1 equivalent of  
epichlorohydrin. 68 g of 1-diphenylmethyl-3-hydroxy-  
azetidine hydrochloride are obtained, i.e. a yield of  
10 51%.

Step 2 : preparation of 1-(4-nitrophenyl)-3-hydroxy-azetidine

According to the procedure of Example 2,  
Step C, starting with 50 g (0.181 mol) of 1-diphenyl-  
15 3-hydroxyazetidinium hydrochloride, 21.2 g of 1-(4-nitro-  
phenyl)-3-hydroxyazetidinium are obtained, i.e. a yield  
of 63%.

Step 3 : preparation of the tartrate salt of  
1-(4-aminophenyl)-3-hydroxyazetidine

20           According to the procedure of Example 2, Step D, starting with 80 g (0.103 mol) of 1-(4-nitrophenyl)-3-hydroxyazetidine, 8.5 g of 1-(4-aminophenyl)-3-hydroxyazetidine are obtained, i.e. a yield of 27%.

Mass spectrum (TSQ 700; ESI-ID):  $m/z = 165$  (MH) +





EXAMPLES	14	15	16	17
[1-(4-aminophenyl)- 3-hydroxy-3-methylazetidide	$6 \times 10^{-3}$ mol	$6 \times 10^{-3}$ mol	$6 \times 10^{-3}$ mol	$6 \times 10^{-3}$ mol
Resorcinol	-	-	0.66	-
1-methyl-4-aminophenol	-	0.74	-	-
1- $\beta$ -hydroxyethyloxy- 2,4-diaminobenzene dihydrochloride	-	-	-	1.45
Dye support	(*)	(*)	(*)	(*)
Demineralized water qs	100 g	100 g	100 g	100 g

Dye support used in the above examples.

- Oleyl alcohol polyglycerolated with 4 mol  
of glycerol, containing 78% active material
- 5 (A.M.) 5.7 g A.M.
- Oleyl alcohol polyglycerolated with 2 mol  
of glycerol 4.0 g
- Oleic acid 3.0 g
- Oleylamine containing 2 mol of ethylene  
oxide, sold under the name Ethomeen 012  
by the company Akzo 7.0 g
- Diethylaminopropyl laurylamino succinamate,  
sodium salt, containing 55% A.M. 3.0 g A.M.
- Oleyl alcohol 5.0 g
- 15 - Oleic acid diethanolamide 12.0 g
- Propylene glycol 3.5 g
- Ethyl alcohol 7.0 g

09890856-110701

- Dipropylene glycol 0.5 g
- Propylene glycol monomethyl ether 9.0 g
- Sodium metabisulphite as an aqueous solution containing 35% A.M. 0.46 g A.M.
- 5 - Ammonium acetate 0.8 g
- Antioxidant, sequestering agent qs
- Fragrance, preserving agent qs
- Aqueous ammonia solution containing 20%  $\text{NH}_3$  10.0 g.

10 At the time of use, each of the compositions is mixed weight-for-weight with 20-volumes aqueous hydrogen peroxide solution (6% by weight), of pH 3. A mixture of pH 9.8 is obtained.

This mixture is applied to natural (BN) or  
15 permanent-waved (BP) grey hair containing 90% white hairs, for 30 minutes.

After rinsing, washing with shampoo, rinsing and drying, each lock is evaluated before and after dyeing in the  $L^*a^*b^*$  system, using a Minolta CM 2002®  
20 spectrophotometer (illuminant D65).

In the  $L^*a^*b^*$  system, the three parameters respectively denote the intensity ( $L^*$ ), the shade ( $a^*$ ) and the saturation ( $b^*$ ). According to this system, the higher the value of  $L$ , the lighter or less intense the  
25 colour. Conversely, the lower the value of  $L$ , the darker or more intense the colour.  $a^*$  and  $b^*$  indicate two colour axes;  $a^*$  indicates the green/red colour axis and  $b^*$  the blue/yellow colour axis.

T020T 958660

The results are given in the table below.

	L*	a*	b*		L*	a*	b*
Ex. 4/BN	40.15	2.6	6.48	Ex. 4/BP	30.89	3.82	4.02
Ex. 5/BN	37.7	4.22	7.74	Ex. 5/BP	30.69	4.95	7.24
Ex. 6/BN	34.18	2.08	-0.35	Ex. 6/BP	27.35	2.34	-1.13
Ex. 7/BN	27.39	-0.49	-12.39	Ex. 7/BP	22.05	1.33	-9.77
Ex. 8/BN	32.12	9.39	-5.19	Ex. 8/BP	24.67	8.51	-6.75
Ex. 9/BN	42.14	3.89	6.29	Ex. 9/BP	33.60	4.57	3.56
Ex. 10/BN	38.39	5.28	9.84	Ex. 10/BP	29.88	5.49	7.85
Ex. 11/BN	32.03	2.62	-1.01	Ex. 11/BP	25.61	2.05	-0.24
Ex. 12/BN	24.06	1.76	-12.70	Ex. 12/BP	20.25	2.41	-8.18
Ex. 13/BN	28.34	10.65	-6.20	Ex. 13/BP	22.49	9.15	-7.04
Ex. 14/BN	41.46	3.20	5.67	Ex. 14/BP	42.44	3.04	4.68
Ex. 15/BN	39.50	4.62	8.70	Ex. 15/BP	30.08	5.35	7.67
Ex. 16/BN	32.06	9.92	-5.58	Ex. 16/BP	33.79	10.54	-5.50
Ex. 17/BN	23.19	1.63	-13.18	Ex. 17/BP	24.93	1.09	-12.41

FOI 95806860